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STUDYING THE MECHANISM OF SCALE FORMATION
IN METAL CORROSION PROCESSES AT HIGH TEMPERATURES

By

A. Bruckman, S. Mrowec, and T. Werber



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STUDYING THE MECHANISM OF SCALE FORMATION IN METAL CORROSION PROCESSES
AT HIGH TEMPERATURES

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Summary

The principles of the application of radioisotope tracers in studying the mechanism of oxidation of metals and alloys are briefly discussed. The results of investigations of sulphide scale layers formation on copper-zinc alloys by the use of zinc and sulphur isotopes are presented.

One of the fields investigating the physico-chemistry of a solid body is the study of oxidation reaction on metals at high temperatures.

The mechanism of these reactions is composed, because of the forma-

tion on the metal surface of a layer of reaction products, which separating substrates from each other causes a further course of the process.

After the first thin layer of the reaction product has been originated, its further course can only take place by the diffusion of substrates through the layer; in the general course of the process the physico-chemical properties of that layer will be decisive. It is evident therefrom, that the study of the oxidation mechanism of metals is reduced first of all to the study of the transportation mechanism of individual reagents in the layer of the reaction product, called scale.

In a series of instances the only method, allowing the tracking of diffusion processes of reagents in scales, is the method based on the application of ray forming indicators.

Many reports have been published /1/,/2/,/3/,/4/, in which the objects of investigation were autodiffusion and heterodiffusion processes carried out on individual reaction products, and not in the tract of their creation process.

Another, less numerous group of investigations /5/,/6/,/7/ are investigations based on processes taking place in the scales at the time of its origination, and thus it contributes directly to the explanation of the reaction mechanism.

The purpose of these investigations is to study the degree of diffusion participation of individual substrates included in the composition of the originating scale. To utilise for this purpose the properties of radiating radioisotopes, it is necessary to introduce in the composition of some of the substrates its isotopes in form of a possibly uniform

decomposed layer, which in time of oxidation will enter into the composition of the scale, and then, by designating the decomposition of activity in the cross section of the originated product, describe in it the concentration of atoms originating from isotope layer, isotopically designated by the reaction.

The marking of radioactivity can also be submitted to the metal / in case of alloy - one of its components, / as well as the oxidation factor.

The introduction of the isotope into the metal, strictly speaking on the surface of the sample, can be obtained by electrolytically covering the sample with a thin metal layer containing its radioactive isotope. In some instances it is possible to apply the ion exchange method between the surface of the metal and the solution of its radioactive salt.

In investigations based on the study of oxidation diffusion / for example S, Br, J / the reaction can be carried out in two stages, introducing the radioactive isotope of the oxidizer into the medium in a certain reaction phase. In this way the obtained scale consists partially of an inactive layer, and partially of a radioactive layer, whose plain delimitation or eventual mutual penetration furnishes information about the occurring diffusion processes.

As has been mentioned, most frequently the object of designations is the decomposition of the concentration of the radiating isotope in the section of the obtained scale. This is obtained, among others ways, by subsequent elimination of scale layers parallel to the surface of scale layers and by measuring either the activity of the removed layers, or of the originated scale. In the investigations carried out by us,

mechanical peeling of layers is applied, by grinding with sand paper or by rolling the surface on a lathe. Grinding with sand paper allows to tear off layers with a thickness of about $5\ \mu$, and lathe rolling of layers to 0.025 mm.

In case of applying an isotope emitting soft rays as for example ^{35}S surface activity dimension of the compound after substitute grindings offers good results, because the large auto-absorption causes, that the detections are based only on particles emitted from the surface layer with a thickness of less than 0.04 mm. But the designation by thus method of a more penetrating radiation / ^{110}Ag , ^{65}Zn , and so on / would be more difficult for interpretation, while the measurement of activity of the material of the collected layer in form of chips gives plainly the value / average activity, / pertaining to the layer of collected thickness.

Mikulski, Mrowec, Stronski and Werber /8/,/9/,/10/,/11/ utilizing the method of two-stage sulfurization has shown, that sulfurization of silver and copper takes place exclusively thanks to the derusting diffusion of the metal, but sulfurization of metals Cu-Zn, Cu-Au and Ag-Zn takes place during simultaneous diffusion of the derusted metal and of the rusting oxidizer. The latter is in partial contradiction with the theoretical model by Wagner /12,/ according to which the process of double layer scale formation on Cu-Zn type alloys should take place exclusively during the derusting diffusion of both metals. If, in the light of quoted experiences during the sulfurization of Cu-Zn alloy, the derusting diffusion of copper appears to be confirmed, by so much does the pre-rusting diffusion of sulfur place under a question mark the axis-

tence of derusting diffusion of zinc. To confirm, whether in the general diffusion process of reagents by scale zinc also participates, the authors undertook a test of applying radiating zinc to investigate the reaction mechanism in a Cu-Zn-S system. The experience was based on the following reasoning. If in the process of increasing in the interior scale layer / on Cu-Zn alloy originates a double layer scale - external, built from copper sulfide and inner, built from a mixture of copper sulfide and zinc sulfide / the derusting diffusion of zinc does take place, while the radiating zinc, introduced by reaction into the surface layer of the alloy, should be situated after the reaction in the whole internal section of the scale layer /5/,/7/. If however, the zinc does not participate in the diffusion process, and the inner scale layer originates thanks to the pre-rusting penetration of the sulfur, then the marked zinc should be situated in the fragment of the inner layer, formed in the initial phase of the oxidation process, in the layer bordering directly with the outer scale layer.

For this experiment samples from Cu-Zn alloy were used, containing up to 9% of Zn. Plates of dimensions of 4 X 3 X 0.3 cm were electrolytically covered by a Cu-Zn layer, containing ^{65}Zn . The thickness of the galvanic coating was 5-10 microns. The composition of the layer varied between 8-10% of zinc. These samples were subjected to sulfurization in liquid sulfur at a temperature of 444°C.

Sulfurization was carried out within 30 and 120 minutes, obtaining a scale of an internal layer thickness of about 0.5 and 1 mm. After the sulfurization was completed, the external scale layers were mechanically

separated. The activity dimension of these layers gave negative results, which is in agreement with the fact, that the outer layer consists exclusively of copper sulfide.

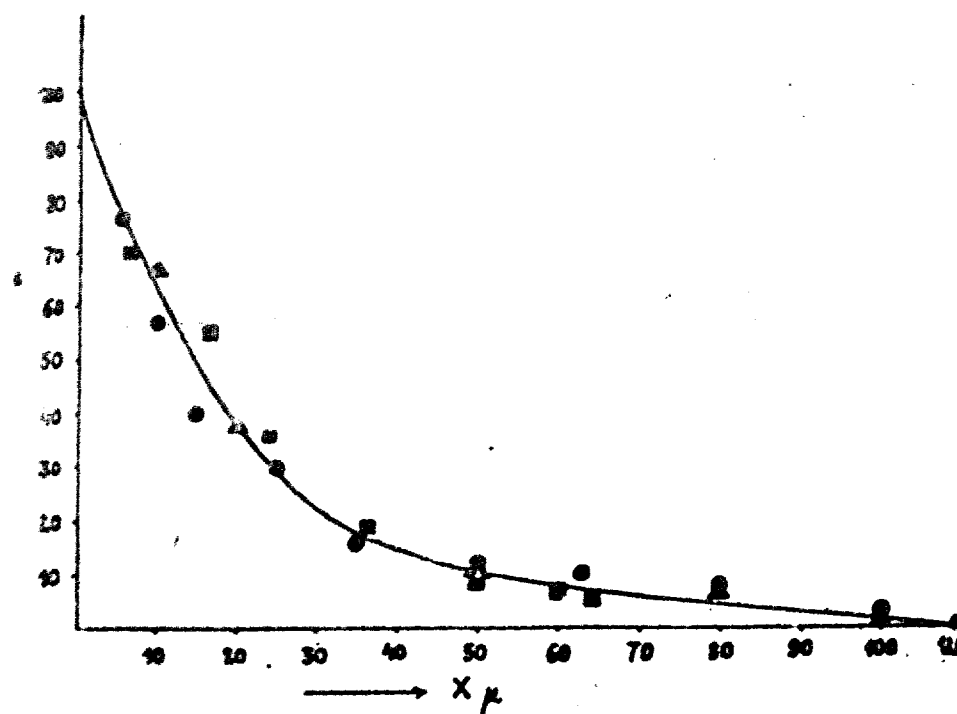


Fig. 1. Relative activity A/A_0 in dependence upon the thickness of the ground substance layer. Δ \blacksquare - sulfur compounds 30 minutes; \bullet - sulfur compounds 120 minutes.

Then, to describe the concentration gradient of the ^{65}Zn isotope in the heterophase internal layer, was carried out a series of alternate activity measurements of that layer, executing each time partial grinding of same with sand papers.

The measurement results are graphically presented at the section / fig. 1, / from which it is evident, that the presence of radiating zinc is practically confirmed in the thickness area of about $50\ \mu$. It can be concluded from above results, that zinc does not practically participate in the general diffusion process of diffusing reagents by the scale, because the presence of the zinc isotope was confirmed only

in a relatively thin layer of inner scale, independent from its total thickness. If in the process of scale increase took part - even in a small degree - the prerusting diffusion of zinc, then in ratio to the increase in scale thickness the range of the presence of the marked zinc would have to subject to an increase.

To further explain the mechanism of oxidation of Cu-Zn type alloys, are presently being conducted investigations over the diffusion of ^{35}S in copper sulfide and silver sulfide, originated on the surface of pure metals, and originated as an outer layer during the sulfurization of alloys of these metals with zinc. These investigations have the purpose of explaining the mechanism of penetration of sulfur through the mentioned scales.

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